Journal of Experimental Nanoscience, 2014
Vol. 9, No. 1, 78–86, http://dx.doi.org/10.1080/17458080.2013.814172

Photocatalytic removal of phenol under visible light irradiation on zinc phthalocyanine/mesoporous carbon nitride nanocomposites

Shu Chin Lee[a], Hendrik O. Lintang[b] and Leny Yuliati[b]*

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, Johor Bahru, Johor, Malaysia;* [b]*Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310, Johor Bahru, Johor, Malaysia*

(*Received 19 March 2012; final version received 06 June 2013*)

A series of zinc phthalocyanine/mesoporous carbon nitride (ZnPc/MCN) nanocomposites was prepared successfully by an impregnation method. The addition of ZnPc (0.05–1.5 wt%) extended the absorption of MCN to longer visible light region without affected its structure. It was found that the photocatalytic activity of the nanocomposites for phenol removal depended on the loading amount of ZnPc. The photocatalytic activity of the MCN increased as the amount of ZnPc increased to 0.05 wt%, but further increase in the loading amount decreased the activity. It was suggested that the optimum amount of ZnPc acted as a good photosensitiser that effectively induced electron charge transfer and reduced the electron-hole recombination.

Keywords: zinc phthalocyanine; mesoporous carbon nitride; visible light; phenol; photosensitiser

1. Introduction

Due to the toxicity of released waste, the management of industrial wastewater is highly concerned nowadays. Phenol can be found in industrial wastewater and has been recognised as one of the organic pollutants, which is very toxic even at low concentration. Various treatment methods have been used to remove phenol, such as adsorption [1–3] and biodegradation.[4–6] While the adsorption method presents drawbacks, such as the need of post-treatment to recover the adsorbent, the conventional biodegradation method is not adequate to treat non-biodegradable wastewaters even though it can be considered as an environmentally friendly way with reasonable cost. Moreover, usually a large amount of micro-organisms and a long residence time are required to degrade the pollutants.[7] Another alternative technology for pollutant removal is the advanced oxidation process (AOP),[7,8] in which the oxidation processes take place by exploiting highly active •OH radicals for the mineralisation of pollutants. Catalytic and photocatalytic oxidation are examples of the AOP techniques.[7–15] Even though the thermal catalytic oxidation of phenol provides milder reaction conditions than the non-catalytic process, reactions conducted under more ambient conditions would be more desired. Photocatalytic oxidation reaction would be one of the best technologies that can solve the problem since it can be conducted at around room temperature. For example, it was reported that TiO_2 was able

*Corresponding author. Email: leny@ibnusina.utm.my

to mineralise phenol under UV light irradiation.[9–11] However, since sunlight only consists of 5% UV light region and more than 40% visible light region, the development of heterogeneous photocatalysis applicable under visible light irradiation is highly needed. Recently, many efforts have been put into the design of visible light-active photocatalysts for organic pollutant removal.[12–15]

On the other hand, mesoporous carbon nitride (MCN) was reported to have a proper band gap energy of 2.7 eV that corresponds to blue light absorption of up to 450 nm.[16] In recent years, MCN has already been used as a photocatalyst for various reactions under visible light irradiation, such as for hydrogen evolution from water splitting [16,17] and selective oxidation of alcohols.[18] The MCN has also been used to treat phenol, such as via adsorption [3] and photocatalytic reaction.[19,20] In order to utilise sunlight in the coming future, the modification of MCN to extend its light absorption to longer wavelength is highly required. In the case of hydrogen evolution reaction, the addition of magnesium phthalocyanines (MgPc) to the MCN was reported to increase the photocatalytic activity of MCN under longer wavelength of visible light region.[21] The addition of zinc phthalocyanines (ZnPc) to the MCN was also reported to extend the light absorption of the MCN to longer visible light region.[22] On the other hand, the incorporation of the ZnPc to titanium oxide (TiO_2) resulted in the absorption of visible light at 500–900 nm, leading to better photocatalytic activity than pure TiO_2 for wastewater decontamination under solar irradiation. [23] In this paper, the effect of ZnPc addition on the properties and photocatalytic activity of MCN for phenol removal under visible light irradiation is discussed in detail.

2. Experimental

The MCN and ZnPc/MCN were prepared in a way similar to that reported in a previous paper [22]. Commercial ZnPc (96%, Acros) was introduced into the prepared MCN via the impregnation method. A certain amount of ZnPc (0.05, 0.10, 0.50, and 1.5 wt% MCN) was dissolved in tetrahydrofuran (99.8%, Lab-Scan Analytical Sciences). The MCN (0.2 g) was added to the solution under continuous stirring at room temperature until the solvent completely evaporated.

Nitrogen adsorption–desorption isotherms were measured at 77 K with a Micromeritics ASAP 2020. The Brunauer—Emmett–Teller (BET) specific surface area and the Barrett—Joyner–Halenda (BJH) pore-size distribution of the samples were determined from the nitrogen adsorption and desorption, respectively. X-ray diffraction (XRD) patterns of MCN and a series of ZnPc/MCN nanocomposites were recorded at room temperature on a Bruker D8 Advance diffractometer using Cu-Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. Diffuse reflectance (DR) visible spectra were measured on a Perkin Elmer Lambda 900 spectrophotometer, in which barium sulphate was used as the reference in these experiments.

Photocatalytic activities of bare MCN and ZnPc/MCN nanocomposites series were evaluated for the removal of phenol under visible light irradiation. Phenol (99.5%, Scharlau Chemie) solution (50 ppm) was prepared using acetonitrile (99.99%, Fischer Scientific) as a solvent. Before the reaction, the sample (50 mg) was dispersed in the solution (50 mL) and stirred under dark conditions for 1 h to establish the adsorption–desorption equilibrium. The mixture was then irradiated with halogen fibre optic illuminator (MI-150, 150 Watt) equipped with an infrared cut-off filter for 6 h. The sample was then separated from the phenol solution by centrifugation and the filtrate was analysed by using

Perkin Elmer Lambda 900 or Thermo Scientific Genesys 10S UV-visible spectrophotometer. In order to investigate the effect of ZnPc on the photocatalytic activity of MCN, a similar photocatalytic reaction experiment was carried out for 24 h under visible light irradiation using a RG610 cut-off filter.

3. Results and discussion

The nitrogen adsorption–desorption isotherm and BJH pore size distribution of the prepared MCN and the series of ZnPc/MCN nanocomposites were measured. As shown in Figure 1, it was confirmed that the MCN and ZnPc/MCN samples have the type IV

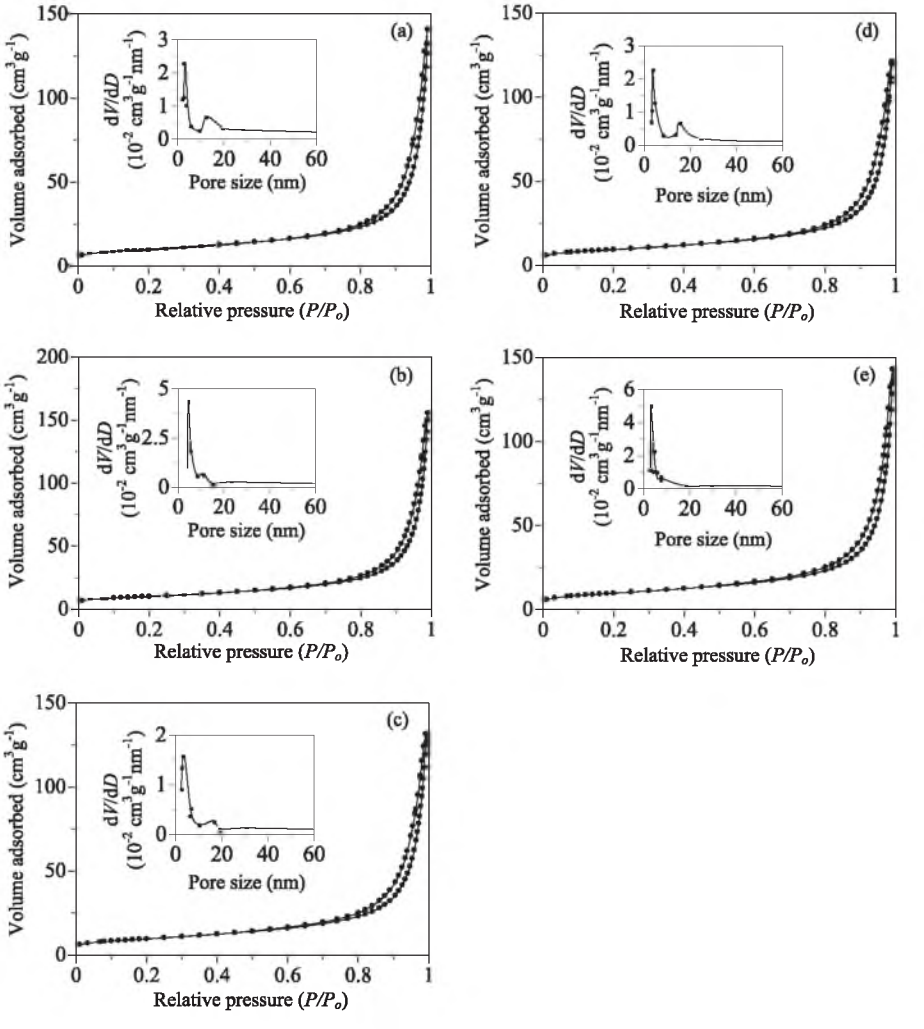

Figure 1. Nitrogen adsorption–desorption isotherms and the corresponding BJH pore size distribution (insets) of (a) MCN and ZnPc/MCN samples with various ZnPc loading amounts of (b) 0.05 wt%, (c) 0.1 wt%, (d) 0.5 wt%, and (e) 1.5 wt%.

isotherm with a hysteresis loop of the H_3 type that corresponded to slit-shaped pore. From the BJH pore size distribution (inset of Figure 1), all samples are bimodal mesoporous materials with average small and large pore sizes of around 3.7 nm and 16.5 nm. The smaller pores as the main pores of MCN may have resulted from the removal of the silica template [20,22], while the larger one may have come from the aggregates of CN owing to the loss of network structure after the removal of the template, as also reported when melamine and glutaraldehyde were used as the precursors.[24] All samples showed similar pore size distribution, except that the larger pores were diminished for the MCN with 1.5 wt% of ZnPc loading. These results clearly suggested that the addition of ZnPc did not block the main pores of MCN, as also supported by the similar BET specific surface area on all samples, which were in the range of 33–36 m^2g^{-1}.

The XRD patterns of unmodified MCN, ZnPc/MCN, and ZnPc powder (ICDD card number of 39-1882) are displayed in Figure 2. It was confirmed that the bare MCN existed in amorphous form. The XRD pattern showed a broad peak at 2θ of 13.0° (d = 0.68 nm) that corresponded to the in-planar distance between nitride pores, and typical (0 0 2) peak at 27.6° (d = 0.32 nm) that corresponded to the graphite-like stacking of the conjugated aromatic units of CN. These results were in good agreement with other literatures reported by other groups.[21,25,26] It was confirmed that the addition of ZnPc did not affect the structure of MCN. When the amount of ZnPc was less than 1.5 wt%, no diffraction peaks of ZnPc were detected, indicating that such a loading amount of ZnPc was too small to be detected by the XRD. On the other hand, a small diffraction peak of ZnPc at 2θ of 6.90°, which can be assigned as (−1 0 1) plane of ZnPc, was observed on the sample with ZnPc loading of 1.5 wt%. It is worth noting that the (−1 0 1) plane was detected on the ZnPc/MCN sample instead of the most pronounced (1 0 1) peak in pure ZnPc, which was observed at 2θ of 9.25°. This would be due to the lack of a perfectly random arrangement of the ZnPc on the MCN. A similar phenomenon on the preferred orientation of ZnPc was also reported when the ZnPc thin film was deposited on silica by the glow discharge-induced sublimation technique.[27]

The absorption properties of mesoporous materials were investigated and the DR visible spectra are displayed in Figure 3. The bare MCN did not absorb light in the long wavelength of the visible region. However, with the addition of ZnPc, a broad absorbance at 500–850 nm was clearly observed. The new absorption in the long visible region indicated

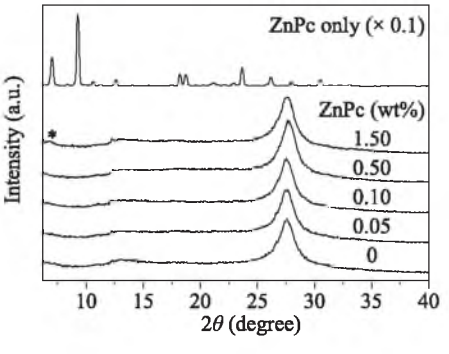

Figure 2. XRD patterns of MCN modified with various amounts of ZnPc. The symbol (*) indicates the diffraction peak of ZnPc. The intensity of the XRD pattern for ZnPc was multiplied by 0.1.

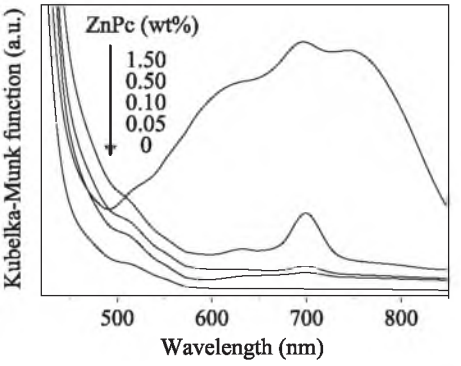

Figure 3. DR visible spectra of MCN modified with various amounts of ZnPc.

the successful impregnation of ZnPc into MCN as well as the excellent properties of the nanocomposite samples to absorb the visible light region at long wavelength, which may enhance the photocatalytic reactions under visible light irradiation. Compared to the absorption peak of pure ZnPc that was reported to be centred at 552 nm due to the Q band absorption related to π–π^* transition [23], the nanocomposite samples showed the Q band absorption in which the centre was red-shifted to 693–698 nm. The red shift would correspond to the change of the environment such as the strong intermolecular interactions, as has also been reported when ZnPc is incorporated into TiO_2 [23] and mesoporous silica.[28] In addition to the red shift, the typical splitting of the Q-band was also observed due to molecular distortion and exciton coupling (Davydov splitting) in the solid phthalocyanine compound.[29] The same effects have been also observed in solid metal phthalocyanines dispersed in various materials.[21,23,28] Since the Q-band absorption is very sensitive to the environment of the ZnPc, the dispersion of ZnPc can be revealed from the analysis of the Q-band.[28] For the ZnPc/MCN sample with ZnPc loading amount of 0.5 wt%, the characteristic monomeric ZnPc peaks can be observed at 629 and 698 nm, suggesting that the sample exists predominantly in the monomeric form. On the other hand, the sample with ZnPc of 1.5 wt% exhibited the spectrum with monomer peaks at 629 and 697 nm and dimer-aggregate peaks at 747 nm as well as unresolved broad peaks in the range of 550–600 nm and 630–660 nm, in good agreement with other literatures.[23,28]

The photocatalytic properties of the ZnPc/MCN were investigated for phenol removal reactions under visible light irradiation. It was confirmed that only a small extent of phenol adsorption (*ca.* 2%) was observed after 6 h in the dark condition. For 6 h-visible light irradiation using halogen fibre optic illuminator ($\lambda > 400$ nm), both MCN and ZnPc/MCN showed catalytic activity, as shown in Figure 4(a). As compared to the bare MCN, the addition of ZnPc with a low loading amount (0.05–0.1 wt%) enhanced the activity (61–62%), but a further increase of ZnPc loading amount (> 0.1 wt%) decreased the activity. It was suggested that when the loading amount of ZnPc was high, the ZnPc covered the surface that inhibited the phenol molecules from being attached to the surface of MCN for reaction, resulting in a drastic decrease in the photocatalytic efficiency. A previous study also reported a similar trend, in which increasing the loading amount of MgPc dye on the MCN photocatalyst gave undesirable activity for the photocatalytic hydrogen

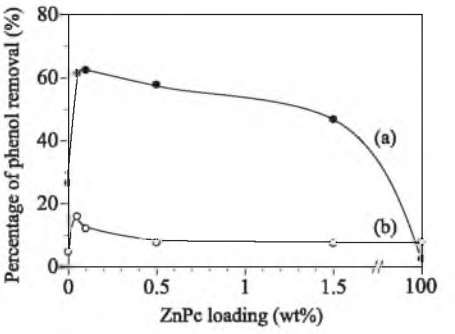

Figure 4. Effect of ZnPc loading amounts on the photocatalytic removal of phenol under visible light irradiation for (a) 6 h without visible light cut-off filter and (b) 24 h with RG610 cut-off filter.

evolution.[21] As also shown in Figure 4(a), the activities of all nanocomposite samples were much higher than those of pure ZnPc and the bare MCN, suggesting the importance of both ZnPc and MCN.

In order to reveal the function of ZnPc, the photocatalytic reactions were also carried out using an RG610 cut-off filter ($\lambda > 610$ nm) for 24 h, as shown in Figure 4(b). Similar to the case of reaction without the cut-off filter, it was obtained that the addition of a small amount of ZnPc (0.05 wt%) increased the photocatalytic activity of MCN (16%). A further increase in the loading amounts decreased the photocatalytic activity, and finally gave a similar level of activity as the pure ZnPc. This result clearly suggested that the role of MCN was less observed and only ZnPc was activated under the light irradiation ($\lambda >$ 610 nm) when the loading of ZnPc was too high. Even though both the reactions gave the same trend of activity, the activities shown were much lower than the ones using visible light without cut-off filter ($\lambda > 400$ nm) (Figure 4(a)). This result was reasonable, as the reaction using the cut-off filter would provide lower energy than that without filter. The lower energy ($\lambda > 610$ nm) would be enough only for electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of ZnPc, which finally transferred to MCN.

Based on the results mentioned above, the function of ZnPc as a photosensitiser to MCN and the reaction mechanism under visible light irradiation can be proposed in Figure 5. MCN showed the valence band (VB) and conduction band (CB) at 1.66 and −1.13 V, respectively [19], while the ZnPc showed HOMO and LUMO levels at 0.42 and −1.58 V, respectively.[30] When the photocatalyst is irradiated by the visible light ($\lambda >$ 610 nm), electrons are excited from HOMO to LUMO of the ZnPc dye. Due to the difference in energy levels, electrons at the LUMO level of ZnPc would be transferred to CB of MCN. As a result, holes on the HOMO level of ZnPc hardly recombine with the electrons, but react with phenol directly, while the electrons accumulated on the CB of MCN will react with the dissolved O_2 from atmosphere to form $\bullet O_2^-$ that will further decompose phenol. On the other hand, under visible light irradiation without filter ($\lambda > 400$ nm), the electron would not only be excited from ZnPc, but also from VB of MCN to its CB. Phenol would be oxidised by holes generated in VB from both charge transfers mentioned above, while electrons in CB react with the dissolved O_2 to form $\bullet O_2^-$ that will further decompose phenol. Therefore, phenol may react with more holes, thus give higher removal percentage. In addition to the higher possibility for phenol to react with the holes, the electron-hole

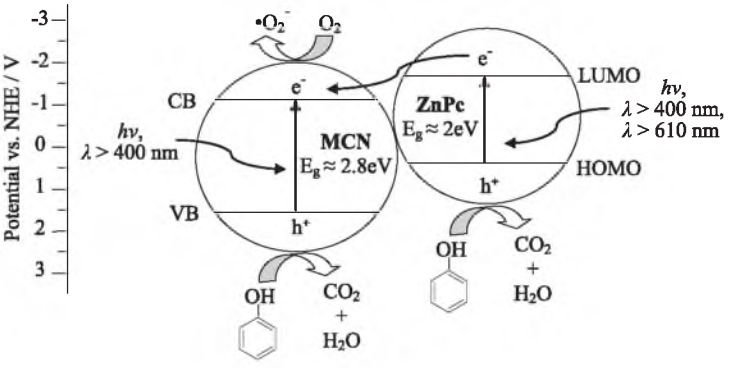

Figure 5. Proposed mechanism of electron-hole transport in ZnPc/MCN photocatalysts for phenol removal under visible light irradiation. The values for the band positions of MCN and ZnPc (~pH 7) were taken from the literatures [19, 30].

recombination rate in the ZnPc could also be reduced when using the ZnPc/MCN, and therefore enhance the catalytic activity.

4. Conclusions

A series of MCN-modified ZnPc was prepared successfully by the impregnation method. The addition of ZnPc extended the absorption of MCN to a long wavelength in the visible region without affecting the surface area and structure of MCN. MCN with the optimum loading amount of 0.05 wt% ZnPc gave high activities of 61 and 16% phenol removal under visible light irradiation after 6-h ($\lambda > 400$ nm) and 24-h ($\lambda > 610$ nm) reactions, respectively. The extended absorption in the long wavelength of visible light as well as the unblocked surface and pores would be the main factors for the high activity of the ZnPc/MCN nanocomposites. It was suggested that both ZnPc and MCN played an important role in the electron-hole transport for the reaction. The optimum amount of ZnPc would act as a sensitiser that induced the electron charge transfer and thus decreased the electron-hole recombination and enhanced the photocatalytic activity.

Acknowledgements

This work was financially supported by the Ministry of Higher Education (MOHE) and Universiti Teknologi Malaysia (UTM) through Flagship Research University Grant (cost center code: Q. J130000.2426.00G07) and Fundamental Research Grant Scheme (cost centre code: R. J130000.7826.4F002). The academy of sciences for the developing world (TWAS) is greatly acknowledged for the gift of Thermo Scientific Genesys 10S UV-visible spectrophotometer via COMSTECH-TWAS joint research grants programme for young scientists (cost centre code: R. J130000.7320.4B039). The authors thank Mr Chiaw Mong Chan (GAT Scientific Sdn. Bhd.) for the nitrogen adsorption–desorption isotherm, BJH pore size distribution, and BET specific surface area measurements. S.C. Lee acknowledges the financial support from MOHE through a MyPhD Scholarship. Part of this work was presented in the International Conference on Enabling Science and Nanotechnology 2012 (ESciNano 2012), © [2012] IEEE, reprinted, with permission, from *2012 International Conference on Enabling Science and Nanotechnology, ESciNano 2012 – Proceedings*, art. no. 6149673.

References

[1] Espósito A, Raffaelli J, Fassino L, Odetti HS, Bottani EJ. Some characteristics of phenol adsorption on activated carbon. J Arg Chem Soc. 2003;91:73–83.

[2] Uddin MT, Islam MS, Abedin MZ. Adsorption of phenol from aqueous solution by water hyacinth ash. J. Eng Appl Sci. 2007;2:11–17.

[3] Haque E, Jun JW, Talapaneni SN, Vinu A, Jhung SH. Superior adsorption capacity of mesoporous carbon nitride with basic CN framework for phenol. J Mater Chem 2010;20:10801–10803.

[4] Chakraborty S, Bhattacharya T, Patel TN, Tiwari KK. Biodegradation of phenol by native microorganisms isolated from coke processing wastewater. J Environ Biol. 2010;31:293–296.

[5] Dey S, Mukherjee S. Performance and kinetic evaluation of phenol biodegradation by mixed microbial culture in a batch reactor. Int J Water Res Environ Eng. 2010;2:40–49.

[6] Lu Y, Yan L, Wang Y, Zhou S, Fu J, Zhang J. Biodegradation of phenolic compounds from coking wastewater by immobilized white rot fungus Phanerochaete chrysosporium. J Hazard Mater. 2009;165:1091–1097.

[7] Liotta LF, Gruttadauria M, Carlo GD, Perrini G, Librando V. Heterogeneous catalytic degradation of phenolic substrates: catalysts activity. J Hazard Mater 2009;162:588–606.

[8] Ahmed S, Rasul MG, Martens WN, Brown R, Hashib MA. Heterogeneous photocatalytic degradation of phenols in wastewater: a review on current status and developments. Desalination. 2010;261:3–18.

[9] Laoufi NA, Tassalit D, Bentahar F. The degradation of phenol in water solution by TiO_2 photocatalysis in a helical reactor. Global Nest J. 2008;10:404–418.

[10] Dixit A, Mungray AK, Chakraborty M. Photochemical oxidation of phenol and chlorophenol by UV/H_2O_2/TiO_2 process: a kinetic study. Int J Chem Eng Appl. 2010;1:247–250.

[11] Wong CL, Tan YN, Mohamed AR. Photocatalytic degradation of phenol using immobilized TiO_2 nanotube photocatalysts. J Nanotechnol. 2011;2011:1–9.

[12] Raji JR, Palanivelu K. Sunlight-induced photocatalytic degradation of organic pollutants by carbon-modified nanotitania with vegetable oil as precursor. Ind Eng Chem Res. 2011;50:3130–3138.

[13] Sun C, Chen C, Ma W, Zhao J. Photodegradation of organic pollutants catalyzed by iron species under visible light irradiation. Phys Chem Chem Phys. 2011;13:1957–1969.

[14] He Z, Xie L, Tu J, Song S, Liu W, Liu Z, Fan J, Liu Q, Chen J. Visible light-induced degradation of phenol over iodine-doped titanium dioxide modified with platinum: role of platinum and the reaction mechanism. J Phys Chem C. 2009;114:526–532.

[15] Long M, Cai W, Cai J, Zhou B, Chai X, Wu Y. Efficient photocatalytic degradation of phenol over Co_3O_4/$BiVO_4$ composite under visible light irradiation. J Phys Chem B. 2006;110:20211–20216.

[16] Wang X, Maeda K, Chen X, Takanabe K, Domen K, Hou Y, Fu X, Antonietti M. Polymer semiconductors for artificial photosynthesis: hydrogen evolution by mesoporous graphitic carbon nitride with visible light. J Am Chem Soc. 2009;131:1680–1681.

[17] Chen X, Jun YS, Takanabe K, Maeda K, Domen K, Fu X, Antonietti M, Wang X. Ordered mesoporous SBA-15 type graphitic carbon nitride: a semiconductor host structure for photocatalytic hydrogen evolution with visible light. Chem Mater. 2009;21:4093–4095.

[18] Su F, Mathew SC, Lipner G, Fu X, Antonietti M, Blechert S, Wang X. mpg-C_3N_4-catalyzed selective oxidation of alcohols using O_2 and visible light. J Am Chem Soc. 2010;132:16299–16301.

[19] Cui Y, Huang J, Fu X, Wang X. Metal-free photocatalytic degradation of 4-chlorophenol in water by mesoporous carbon nitride semiconductors. Catal Sci Technol. 2012;2:1396–1402.

[20] Lee SC, Lintang HO, Yuliati L. A urea precursor to synthesize carbon nitride with mesoporosity for enhanced activity in the photocatalytic removal of phenol. Chem Asian J. 2012;7:2139–2144.

[21] Takanabe K, Kamata K, Wang X, Antonietti M, Kubota J, Domen K. Photocatalytic hydrogen evolution on dye-sensitized mesoporous carbon nitride photocatalyst with magnesium phthalocyanine. Phys Chem Chem Phys. 2010;12:13020–13025.
[22] Lee SC, Lintang HO, Yuliati L. Synthesis and characterization of zinc phthalocyanine/mesoporous carbon nitride nanocomposites. Adv Mater Res. 2012;364:363–367.
[23] Machado AEH, França MD, Velani V, Magnino GA, Velani HMM, Freitas FS, Müller PS, Jr., Sattler C, Schmücker M. Characterization and evaluation of the efficiency of TiO_2/zinc phthalocyanine nanocomposites as photocatalysts for wastewater treatment using solar irradiation. Int J Photoenergy. 2008;2008:1–12.
[24] Shen W, Ren L, Zhou H, Zhang S, Fan W. Facile one-pot synthesis of bimodal mesoporous carbon nitride and its function as a lipase immobilization support. J Mater Chem. 2011;21:3890–3894.
[25] Goettmann F, Fischer A, Antonietti M, Thomas A. Chemical synthesis of mesoporous carbon nitrides using hard templates and their use as a metal-free catalyst for Friedel-Crafts reaction of benzene. Angew Chem Int Ed. 2006;45:4467–4471.
[26] Groenewolt M, Antonietti M. Synthesis of g-C_3N_4 nanoparticles in mesoporous silica host matrices. Adv Mater. 2005;17:1789–1792.
[27] Maggioni G, Manera MG, Spadavecchia J, Tonezzer M, Carturan S, Quaranta A, de Julián Fernández C, Rella R, Siciliano P, Della Mea G, Vasanelli L, Mazzoldi P. Optical response of plasma-deposited zinc phthalocyanine films to volatile organic compounds. Sensor Actuat B. 2007;127:150–156.
[28] Subbiah S, Mokaya R. Synthesis of transparent and ordered mesoporous silica monolith films embedded with monomeric zinc phthalocyanine dye. Chem. Commun. 2003;860–861.
[29] Mizuguchi J, Matsumoto S. Molecular distortion and exciton coupling effects in β metal-free phthalocyanine. J Phys Chem A. 1999;103:614–616.
[30] Giraudeau A, Fan F-RF, Bard AJ. Semiconductor electrodes. 30. Spectral sensitization of the semiconductors titanium oxide (n-TiO_2) and tungsten oxide (n-WO_3) with metal phthalocyanines. J Am Chem Soc. 1980;102:5137–5142.